

CATALYTIC OXIDATION OF METHANOL TO FORMALDEHYDE

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

56887

By
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to the
DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
DECEMBER, 1978

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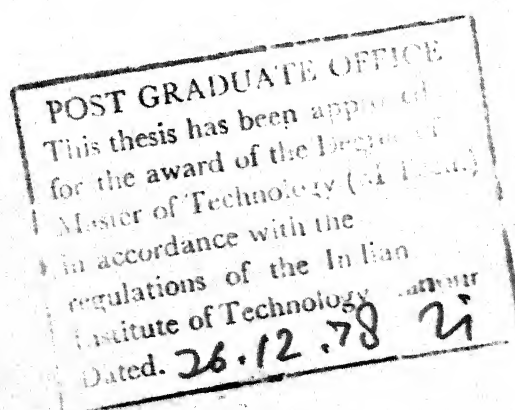
CERTIFICATE

It is certified that this work 'CATALYTIC OXIDATION OF METHANOL TO FORMALDEHYDE' has been carried out under my supervision and that this has not been submitted elsewhere for a degree.

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ACKNOWLEDGEMENTS

The author wishes to express his deep appreciation to Professor R.D. Srivastava for his valuable guidance and advice, and for his close supervision and constant encouragement at all stages of this investigation.

Thanks are also due to all friends who have extended their assistance at hours of need, particularly Messrs R.K. Sharma, R.M. Athappan and Ran Mohan.

Finally, thanks are due to Mr. B.S. Pandey for his excellent typing and to Mr. D.S. Panesar for tracing the drawings.

Author

CONTENTS

	List of Tables	...	v
	List of Figures	...	vi
	Abstract	...	vii
CHAPTER			
1	INTRODUCTION	...	1
	1.1 Literature Survey	...	1
	1.2 Present Work	...	4
2	EXPERIMENTAL	...	5
	2.1 Materials	...	5
	2.2 Apparatus	...	5
	2.3 Method of Catalyst Preparation		8
	2.4 Experimental	...	9
	2.5 Analytical Procedure	...	10
3	RESULTS AND DISCUSSION	...	12
	3.1 Effect of Catalyst Composition		13
	3.2 Effect of Temperature	...	13
	3.3 Effect of W/F Ratio and Methanol Concentration	...	17
	3.4 Effect of Diffusion	...	17
	3.5 Kinetic Analysis	...	24
	3.6 Temperature Effect on Rate Constants		31
4	CONCLUSION	...	38
	REFERENCE	...	39
	NOMENCLATURE	...	41

LIST OF TABLES

TABLE		PAGE
1	Surface Areas of the Samples	16
2	Two Stage Redox Models	28
3	Results of Regression Analysis	29
4	Comparison Between the Experimental and Calculated Data	32

LIST OF FIGURES

FIGURE		PAGE
1	Experimental Set-up ...	6
2	Effect of Catalyst Composition on Conversion, Yield: $W/F = 35.0$, Temp. = 400°C , 11 per cent Methanol in Air	14
3	Effect of Temperature on Conversion and Selectivity for $W/F = 60.0$ gm hr/mole and 10 per cent methanol in Air	15
4	Effect of W/F on Conversion of Methanol for Various Methanol Concentrations in the Feed Mixture at 300°C ...	18
5	Effect of W/F on Conversion of Methanol for Various Methanol Concentrations in the Feed Mixture at 325°C ...	19
6	Effect of W/F on Conversion of Methanol For Various Methanol Concentrations in the Feed Mixture at 350°C ...	20
7	Effect of W/F on Conversion of Methanol for Various Methanol Concentrations in the Feed Mixture at 375°C ...	21
8	Effect of W/F on Conversion of Methanol for Various Methanol Concentration in the Feed Mixture at 400°C ...	22
9	Effect of Feed Velocity on Percentage Conversion of Methanol at 350°C , 10 per cent Methanol in Air, $W/F = 40.0$ gm. mole/hr.	23
10	Initial Ratio (r_0) VS Mole Percentage Methanol in Air ...	25
11	Temperature Effect on Rate Constant k_1	34
12	Temperature Effect on Rate Constant k_2	35

ABSTRACT

The kinetics of oxidation of methanol to formaldehyde over vanadium pentoxide - potassium sulphate supported on silica gel catalyst was investigated between 300°C to 400°C at atmospheric pressure. The catalyst 15 per cent V_2O_5 , 20 per cent K_2SO_4 , and 65 per cent silica gel, was found to be optimum in terms of conversion and selectivity to formaldehyde. The following rate expressions, deduced assuming a steady state involving simultaneous reduction of catalyst by methanol and oxidation of the catalyst to the original state by gaseous oxygen, represents the experimental data satisfactorily:

$$r = \frac{k_1 p_M}{\left[1 + \frac{k_1 p_M}{2k_2 p_{O_2}^{0.5}} \right]}$$

The activation energies of the two steps were 14.80 and 16.64 KCal/mole, respectively.

CHAPTER 1

INTRODUCTION

Formaldehyde is an industrially important organic chemical used in the production of resin and polymers and numbers of formaldehyde products [1]. The properties which makes formaldehyde of value are due principally to its high order of chemical reactivity, its colorless nature, its stability and the purity of its commercial forms. The term formaldehyde products signify those products which include formaldehyde solution, paraformaldehyde and hexamethylenetetramine. The commercial production on a large scale was started when the silver-catalyst process was patented. This involves combined dehydrogenation and oxidation reaction over metallic silver catalyst at about 600°C [2].

A brief literature survey on the kinetics of oxidation of methanol is presented below.

1.1 Literature Survey:

The oxidation of methanol with air over iron, molybdenum and iron molybdenum oxides at 300 to 700°C was studied by Adkins and Peterson in 1931 [3]. A weak methanol air mixture was used and formaldehyde was formed by the oxidation of methanol at temperature around 350°C .

The main advantage of the oxide catalyst process over the silver catalyst are [4]

- (i) higher yield
- (ii) higher resistance to poisoning
- (iii) longer life of catalyst
- (iv) less fire or explosion hazards in the plant due to low methanol concentration.

Boreskov [5] investigated the kinetics of methanol oxidation over $\text{Fe}_2\text{O}_3\text{-MoO}_3$ at 275°C . Jiru [6] also studied on the same catalyst and rate of the oxidation of methyl alcohol at a temperature of 270°C is given by the expression

$$r = \frac{k_1 p_M}{1 + 0.5(k_1/k_2) \left(\frac{p_M}{p_{O_2}}\right)}$$

Pernicone and coworkers [7] studied the mechanism over $\text{MoO}_3\text{-Fe}_2(\text{MoO}_4)_3$ catalyst. The kinetics of methanol oxidation over $\text{MoO}_3\text{-Fe}_2(\text{MoO}_4)_3$ catalyst was studied by means of a differential flow reactor and a pulse reactor in the temperature range $180\text{-}280^\circ\text{C}$.

Mann and Hahn [8] studied the kinetics of methanol oxidation over manganese dioxide - molybdenum trioxide catalyst in an integral flow reactor between $250\text{-}460^\circ\text{C}$. The rate expression

$$r = \frac{k_1 p_M}{1 + \frac{k_1 p_M}{2k_2 (p_{O_2})^{1/2}}}$$

was derived assuming a steady state involving a two stage irreversible oxidation reduction process.

Mann and Dosi [9] investigated the kinetics of vapor phase catalytic air oxidation of methanol to formaldehyde over vanadium pentoxide-molybdenum trioxide between 250 and 530°C at atmospheric pressure and the effect of several process variable on the conversion of methanol and the selectivity of the catalyst for formaldehyde were determined. The rate expression

$$r = \frac{k_1 p_M}{1 + \frac{k_1 p_M}{2k_2 (p_{O_2})^{1/2}}}$$

was derived which represented the data very satisfactorily.

Mann, Jain and Dosi [10] also studied recently the vapor phase oxidation of methanol to formaldehyde over molybdenum oxide, tungsten oxide and their mixtures.

Bhattacharya [11] studied the kinetics of this oxidation reaction at 246°, 264° and 281°C at low conversion in a flow reactor using pure vanadium pentaoxide catalyst. The following rate equation, deduced assuming a steady state involving simultaneous reduction of catalyst by methanol and oxidation of the catalyst to the original state by gaseous oxygen, represented the experimental data

$$r = \frac{2k_1 k_2 p_M p_{O_2}}{k_1 p_M + 2k_2 p_{O_2}}$$

Trama [12] studied the structure of the catalyst of $V_2O_5 - MoO_3$ and $V_2O_5 - K_2SO_4$ system, by x-ray, infrared, ESR and magnetic susceptibility measurements and found that both MoO_3 and K_2SO_4 has promotional action on vanadium pentaoxide for oxidation reaction. Recently, Agarwal [13] studied the kinetics of this reaction over 10 per cent V_2O_5 , 20 per cent K_2SO_4 and 70 per cent silicagel between $330-410^\circ C$. However, no detailed information is available as yet regarding the promotional action of potassium on V_2O_5 for the oxidation of methanol to formaldehyde.

1.2 Present Work:

In this investigation, kinetics studies of the oxidation of methanol catalysed by $V_2O_5 - K_2SO_4$ in varied compositions were made by means of fixed bed reactor at atmospheric pressure. The effect of a number of variables on the conversion of methanol to formaldehyde and yield were determined and a rate expression which might be used effectively for industrial reactor design was derived.

The purpose of this study was to obtain some understanding of the catalytic activity of the $V_2O_5 - K_2SO_4$ system and to examine the possibilities of interpreting the mechanism. The experimental results are analysed on the basis of two stage redox kinetics with statistical data interpretation.

CHAPTER 2

EXPERIMENTAL

2.1 Materials:

Methanol, ammonium meta vanadate and potassium sulphate were the prime materials used herein. These chemicals were obtained from Sarabhai M. Chemicals, Reanál (Hungary) and Sarabhai M. Chemicals, respectively.

2.2 Apparatus:

A general schematic diagram of the experimental set-up is given in Figure 1.

It consists of small air compressor, drying and purifying towers for air, control valves, flow meters, a preheater for the reactant mixture, condensers for the products and the most important, the reactor. Temperatures at various point along the reactor were measured with the iron-constantan thermocouples.

2.2.1 Methanol Vaporizer:

Methanol was vaporized in 1/2 in. O.D. tube which were wrapped with insulating heating tape to achieve the preheater temperature.

2.2.2 Salt Bath:

It is a 300 kg capacity cylindrical tank 50 cm a long and 56 cm O.D. made of stainless steel. The tank was made

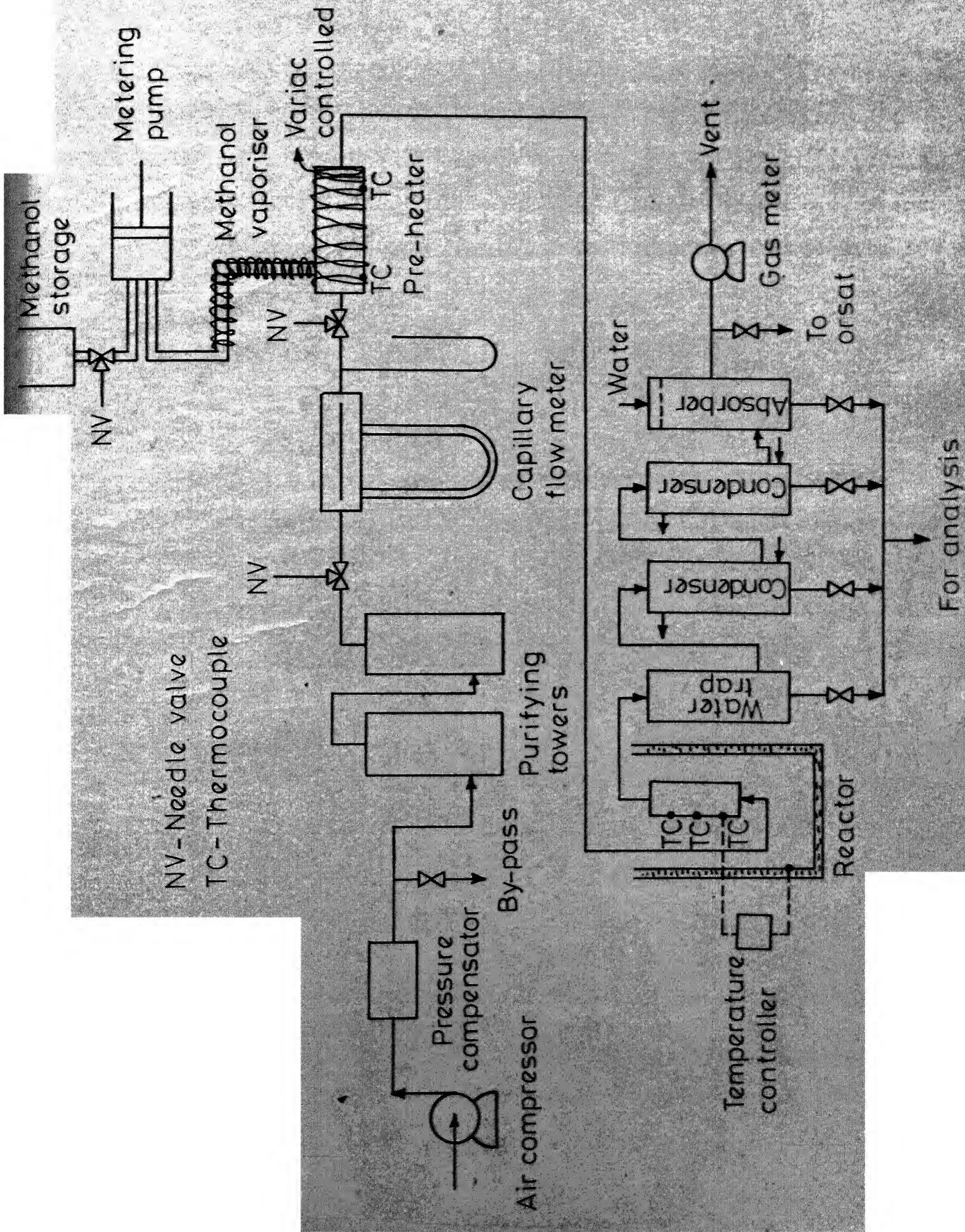


Fig. 1 - Experimental set-up.

of a double wall filled with glass wool layer to reduce heat loss. A sandwich of asbestos cloth 3 mm thick and glass wool in between was used to minimise heat loss. A 1/2 in. O.D. asbestos rope was carefully wrapped along the cylindrical vessel to reduce radiation loss. Tank was filled with fused inorganic salt mixture of composition

KNO_3	53 per cent
NaNO_3	7 per cent
NaNO_2	40 per cent

which having a melting point of 404.3°K . This mixture is non-toxic and chemically stable up to 727°K in the absence of any contaminants. At about 800°K which is maximum operating temperature, the salt undergoes a slow decomposition largely a thermal breakdown of nitrite to nitrate. Salt mixture was heated by an electric immersion heater of 3KW capacity supplied by Escorts India Limited, India. Iron-constantan thermocouples fitted in stainless tube of bore diameter 4 mm was dipped in the salt mixture for the temperature measurement.

2.2.3 Flow Meters:

The calibrated capillary flow meter, capillary size of 6 mm O.D. was used to measure the flow rate of air.

2.2.4 Purifiers and Driers:

Air was passed through a series of drier and purifier containing fused calcium chloride and potassium hydroxide pellets.

2.2.5 Condensers:

Two double walled condensers were used in series to condense the product gases. Chilled water was circulated through the condenser to ensure complete condensation of products.

2.2.6 Preheater:

It is 3/4 in. O.D. stainless steel pipe of 2' length. Preheater was welded to inlet methanol vapor 1/2 in. O.D. tube. This is again connected to air line by a 1/4 in. stainless steel tube. Heating tape was wrapped all along the preheater and temperature was controlled by a variac.

2.2.7 Reactor:

It is of a fixed bed type, consisting of a 1 in. diameter 6 in. long stainless steel tube. A wire mesh was welded at the bottom of the reactor for the catalyst support. Nuts and bolts were used to fasten the reactor to outlet pipe. Compressed gasket of 3 mm thickness was used. A wire mesh was placed at top of the reactor to prevent the loss of catalyst with the products. The temperature along the reactor height will be measured at two different point to check any thermal gradients during the reaction. The reactor temperature will be controlled to within ' $\pm 5^{\circ}\text{C}$ '.

2.3 Method of Catalyst Preparation:

For the catalyst preparation the technique of impregnating an active component on an inactive support was used. For our

system the impregnating solution will be a mixture of vanadium pentoxide and potassium sulphate and support was silica gel.

Calculated amount of ammonium meta vanadate was taken in 100 ml beaker and a thick paste was made in distilled water. In another beaker a saturated solution of oxalic acid was made in distilled water and was heated to 70-75°C. The oxalic acid solution was added with constant stirring. In no case the temperature was allowed to rise above 75°C in order to prevent decomposition of vanadium pentoxide. During the process vanadium oxalate solution was formed and carbon dioxide gas was evolved. The color of solution changed from green to deep blue indicating completion of reaction and no V_2O_5 was left unreacted. A weighed amount of potassium sulphate was added to vanadium oxalate solution. The resulting solution was added to silica gel with constant stirring.

Impregnated vanadium pentoxide and potassium sulphate on silica gel was dried on a vacuum drier at 70°C for at least 8 hrs. The catalyst was calcined at 500°C for 6 hours and activated at 600°C.

2.4 Experimental Procedure:

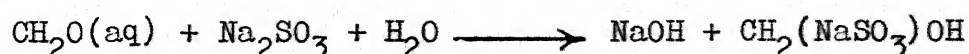
The reactor will be filled with a predetermined quantity of the catalyst using wire mesh below and above the catalyst bed. To have a uniform temperature of reactant just before the catalyst bed, porcelain beads will be used. The required

flow of methanol and air will be adjusted using a metering pump and a needle valve respectively. The mixture will be preheated and the product gases will be cooled using chilled water condensers. The gases will be made to pass through a water trap to condense heavier products. All the experimental runs will be taken under steady state condition (requiring nearly 3 hours after preliminary adjustments). The lighter gaseous products, carbon dioxide, carbon monoxide passed through Orsat apparatus. The gaseous products were analysed intermittently.

2.5 Analysis of the Product:

2.5.1 Formaldehyde Estimation:

Sodium sulphite method [14] was used to estimate formaldehyde. The method is based on the quantitative liberation of sodium hydroxide when formaldehyde reacts with sodium sulphite to form the formaldehyde bisulphite addition product.

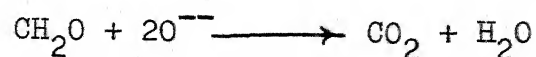
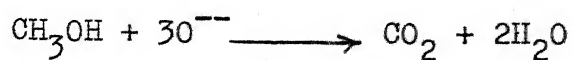


$$\text{Percent Formaldehyde} = \frac{\text{Acid titer} \times \text{Normality of acid} \times 3.003}{\text{Weight of sample}}$$

2.5.2 Methanol Estimation:

The chemical procedure of Blank and Finkenbeiner [15] was used. In this procedure, the formaldehyde solution is completely oxidized by a measured excess of chromic acid and the consumption of oxidizing agent determined by titrating

the unreacted chromic acid with a standard iodine solution. Under the test conditions, the oxidation reactions take place as indicated in the following equations:



$$\begin{aligned} \text{Per cent Methanol} &= (\text{Blank titer} - \text{sample titer}) \times \text{Normality} \times 21.33 \\ &\quad - (0.7114 \times \text{per cent HCHO}) - (0.232 \times \text{per cent HCOOH}) \end{aligned}$$

2.5.3 Carbon dioxide and Carbon monoxide Estimation:

The usual Orsat apparatus was used to determine its concentration. The gas was passed through a series of absorption tube containing potassium hydroxide and ammonical solution of cuprous chloride.

The contents of component on the gas mixture was calculated by reduction in volume of the gas after each absorption process. The quantitative composition of gas mixture was expressed as percentage volume.

CHAPTER 3

RESULTS AND DISCUSSION

Experimental data were obtained by means of quasi-isothermal fixed bed reactor. The steady state was not only realized from the operational conditions but also from the product analysis. The effect of various variables, namely, methanol: air mixture in the feed mixture, reaction temperature, T , and the ratio of the catalyst weight to the methanol feed rate, W/F , on the conversion, X , selectivity, S , of the catalyst for formaldehyde formation and the yield of the formaldehyde, Y , were investigated.

$$\text{Conversion (per cent)} = \frac{\text{Moles of methanol reacted per hour}}{\text{Moles of methanol fed per hour}} \times 100$$

$$\text{Yield (per cent)} = \frac{\text{Moles of formaldehyde formed per hr.}}{\text{Moles of methanol fed per hour}} \times 100$$

$$\text{Selectivity (per cent)} = \frac{\text{Moles of formaldehyde formed per hour}}{\text{Moles of formaldehyde formed per hour} + \text{Moles of carbon oxides formed per hr.}} \times 100$$

$$\text{Rate of reaction} = \frac{\text{Moles of methanol reacted}}{(\text{hr.}) (\text{gm of catalyst})}$$

The activity of catalyst remained fairly constant during the course of investigation. No reaction between methanol and air was observed to take place in the absence of the catalyst even after 3 hours at 400°C .

Reference to the various samples will be made giving their composition as weight per cent V-K, hence V-15-K-20 means a sample of V_2O_5 - K_2SO_4 supported on silica gel having 15 per cent of the active element as V_2O_5 and 20 per cent of the promoter K_2SO_4 .

The reciprocal space velocity (W/F) was changed by changing the methanol feed rate i.e. F and keeping the weight of the catalyst charged into reactor constant.

3.1 Effect of Catalyst Composition:

Figure 2 shows the effect of catalyst composition on the conversion and yield at 400°C with 11 per cent methanol in the feed and $W/F = 35.0 \text{ gm hr/gm. mole}$. Although, the conversion remains about 80 per cent for V-10 but yield is low for all values of K and for V-15 conversion and yield remains high for all value of K. Hence V-15-K-20 was chosen to be an optimum catalyst for the further kinetic study. It is interesting to note that surface areas are also consistent for various vanadium samples with K-10 composition (Table 1).

3.2 Effect of Temperature:

Figure 3 shows the effect^{of} temperature on conversion and selectivity of the catalyst (V-15-K-20) in the temperature between 300 - 400°C and W/F of 60.0 gm hr/mole for 10 per cent methanol in air. The conversion of methanol increases upto 80 per cent as the temperature increased. The selectivity of

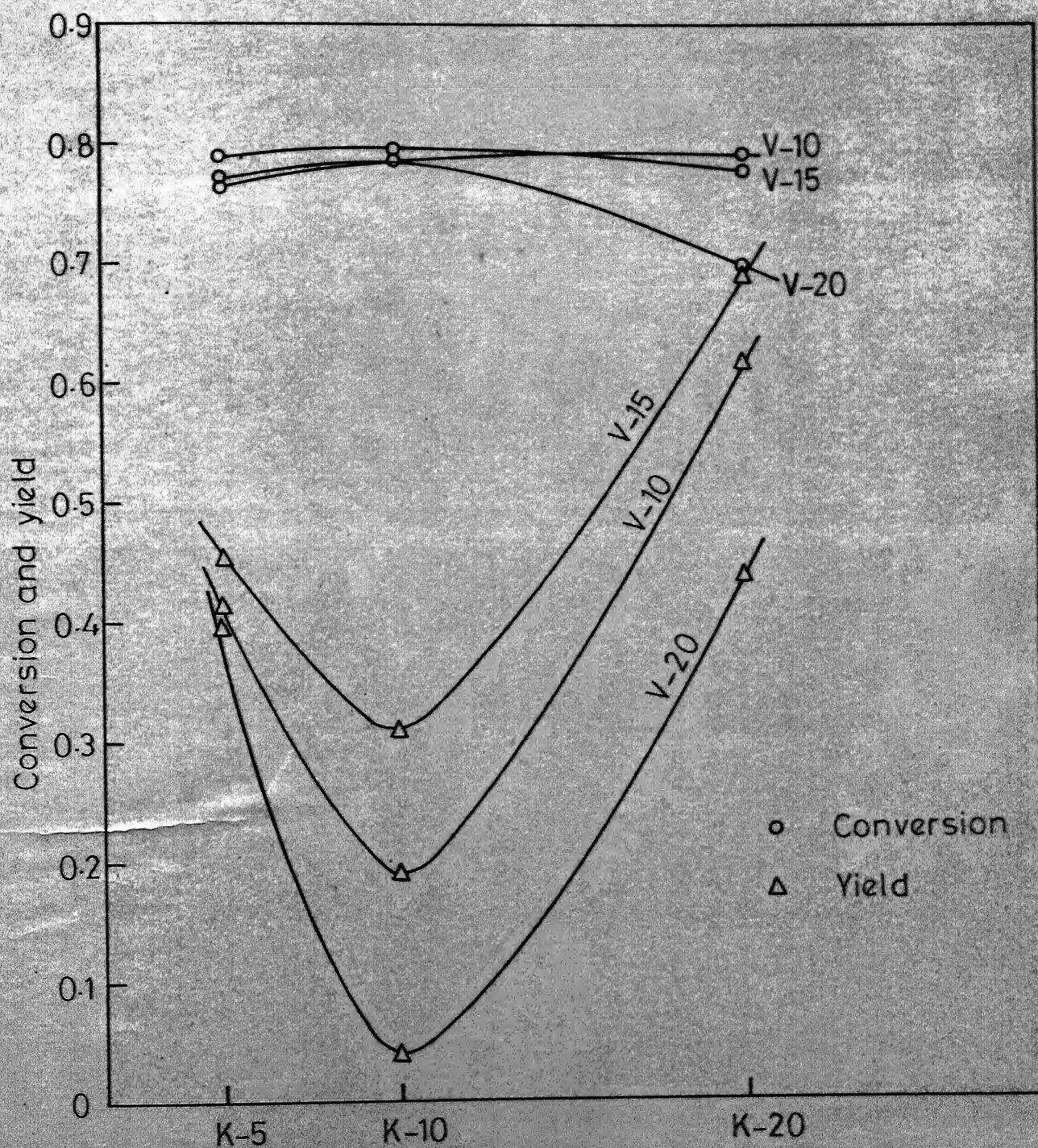


Fig. 2 - Effect of catalyst composition on conversion and yield $W/F = 35.0$ gm-hr/mole, Temperature = 400°C , 11% methanol in air.

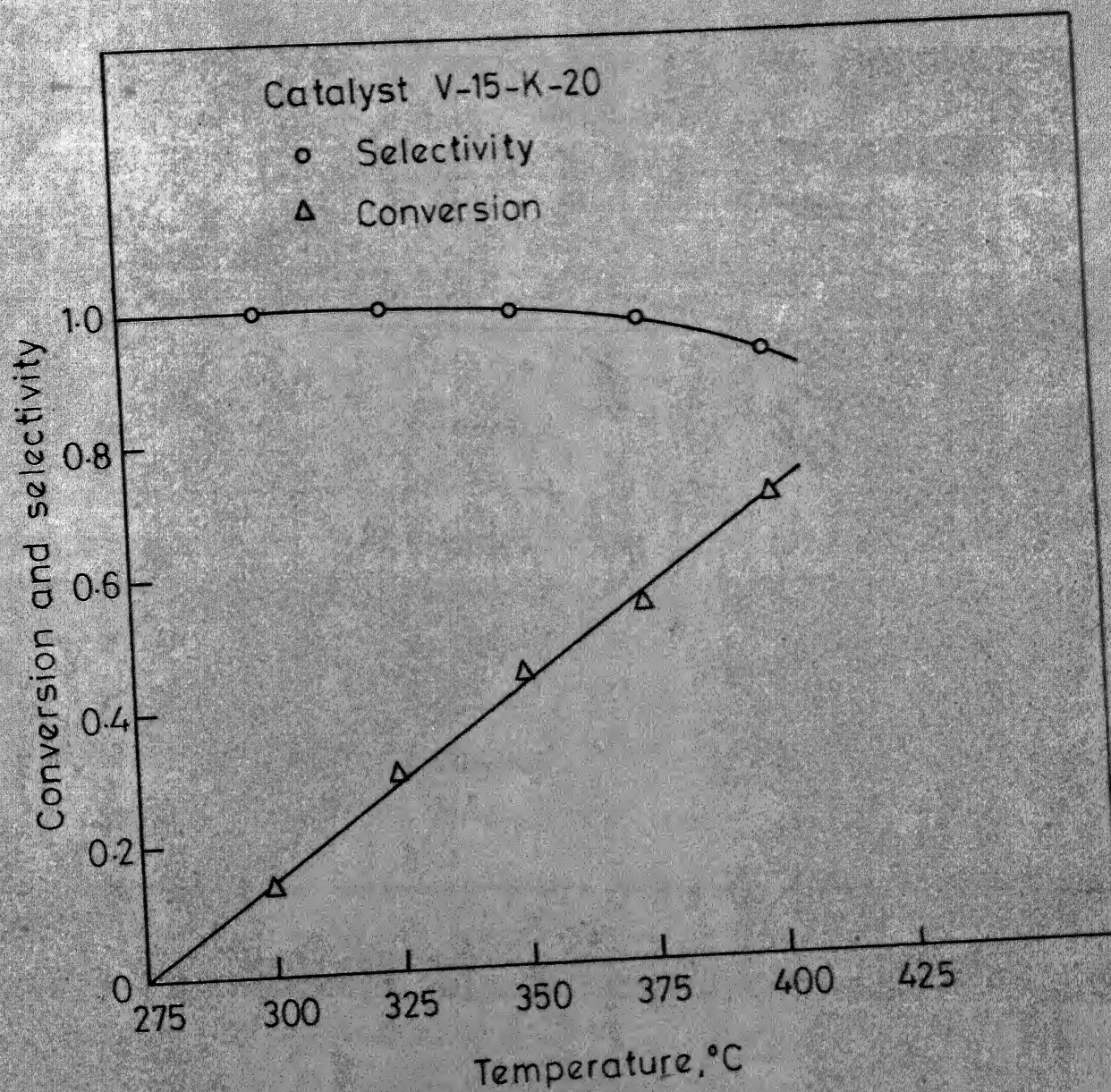


Fig. 3 - Effect of temperature on conversion and selectivity for $W/F = 60.0$ gm-hr/mole and 10% methanol in air

TABLE 1
SURFACE AREA OF THE SAMPLES

S.No.	Catalyst Composition	Surface Area, m ² /gm
1	V-10-K-5	19.4
2	V-10-K-10	13.0
3	V-10-K-20	15.0
4	V-15-K-5	12.2
5	V-15-K-10	7.0
6	V-15-K-20	16.0
7	V-20-K-5	8.2
8	V-20-K-10	2.8
9	V-20-K-20	18.0

the catalyst was 100 per cent at lower temperature but decreased as the reaction temperature increased.

3.3 Effect of W/F Ratio and Methanol Concentration:

Figures 4-8 show the effect on conversion with varying concentration of methanol between 8 and 12 per cent at the temperature of 300°C, 325°C, 350°C, 375°C and 400°C respectively.

For all methanol concentration, increase in W/F increased the conversion of methanol. This confirms with the fact that increase in W/F ratio with constant feed gas flow rate and methanol feed concentration results in increased contact time. At any given value of W/F, conversion of methanol increased with higher methanol concentration in the feed.

3.4 Effect of Diffusion:

The affects of diffusion were kept to a minimum by using a high velocity of the gas, and to test if external diffusion will effect on kinetic results, the method suggested by Corrigan [16] was followed. Some of the significant runs were redone with keeping W/F constant but reducing F and consequently W.

Figure 9 shows the effect of feed velocity on conversion of methanol. The fair constancy of the conversion obtained by changing the feed rate while keeping W/F constant suggested that the diffusion of gases was not controlling the rate and possibility of diffusion in the pores controlling the reaction rate was eliminated by using small particle size of the catalyst. (-30+40 mesh size)

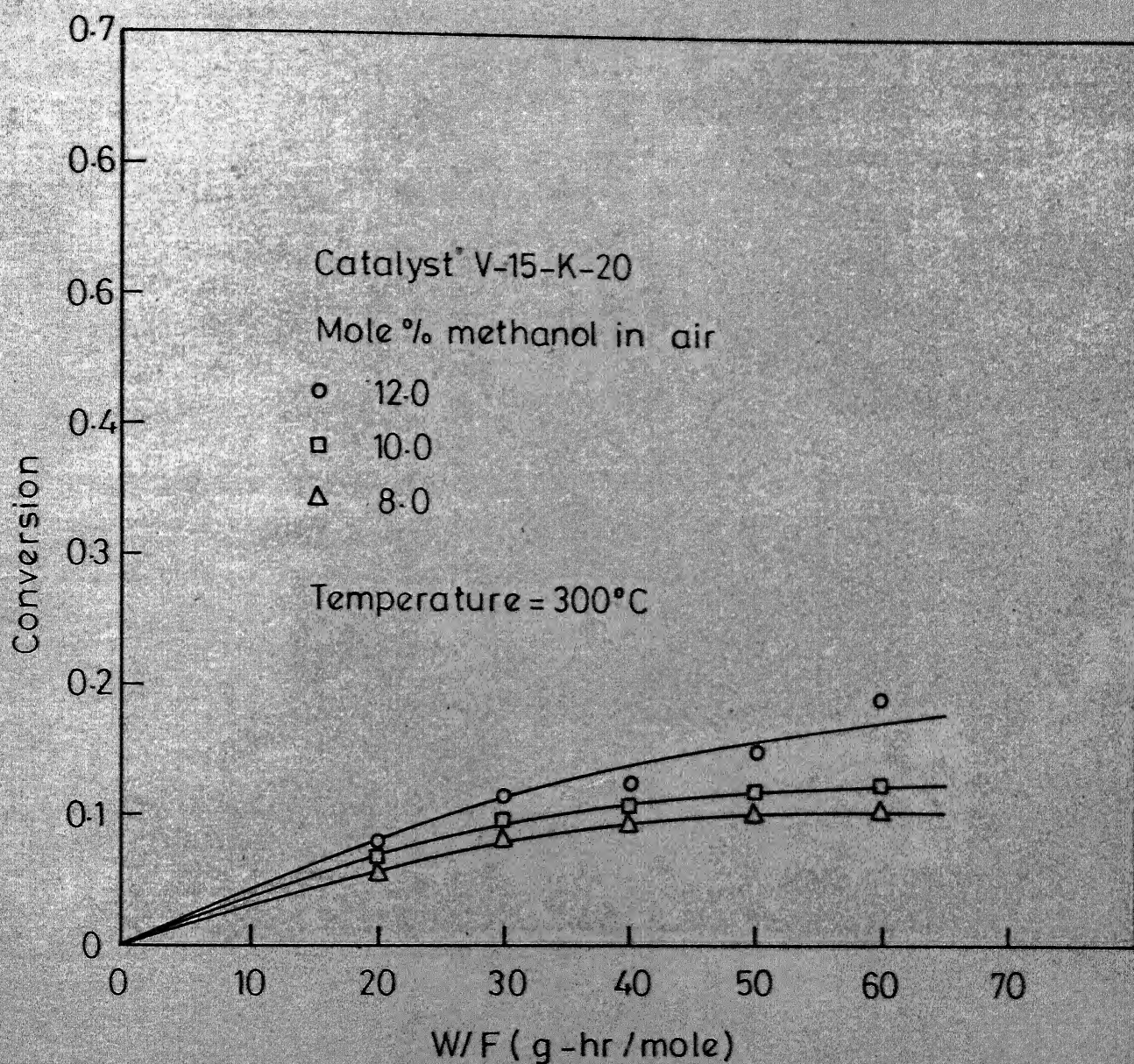


Fig. 4 - Effect of W/F on conversion of methanol for various methanol concentrations in the feed mixture.

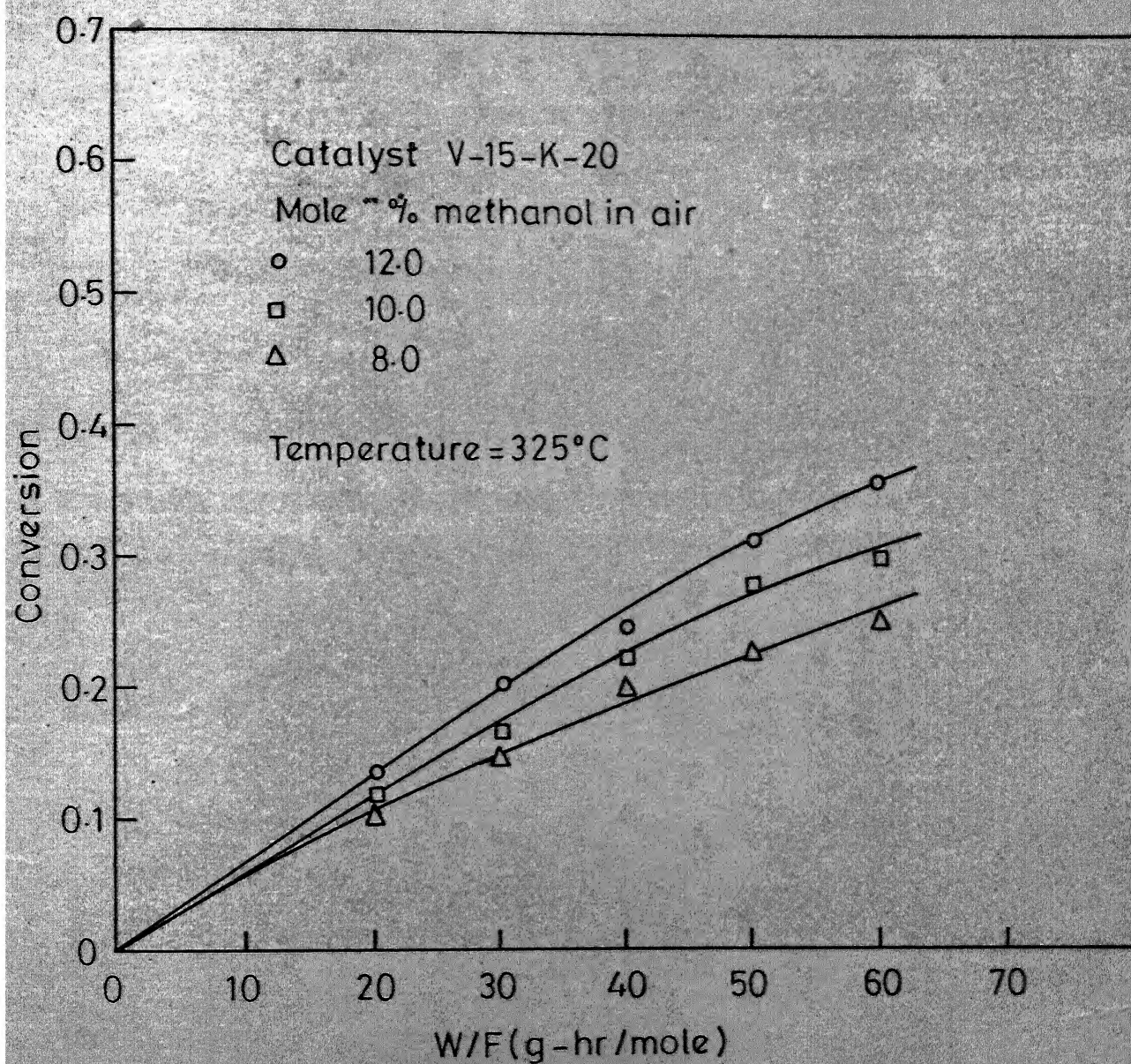


Fig. 5 - Effect of W/F on conversion of methanol for various methanol concentrations in the feed mixture.

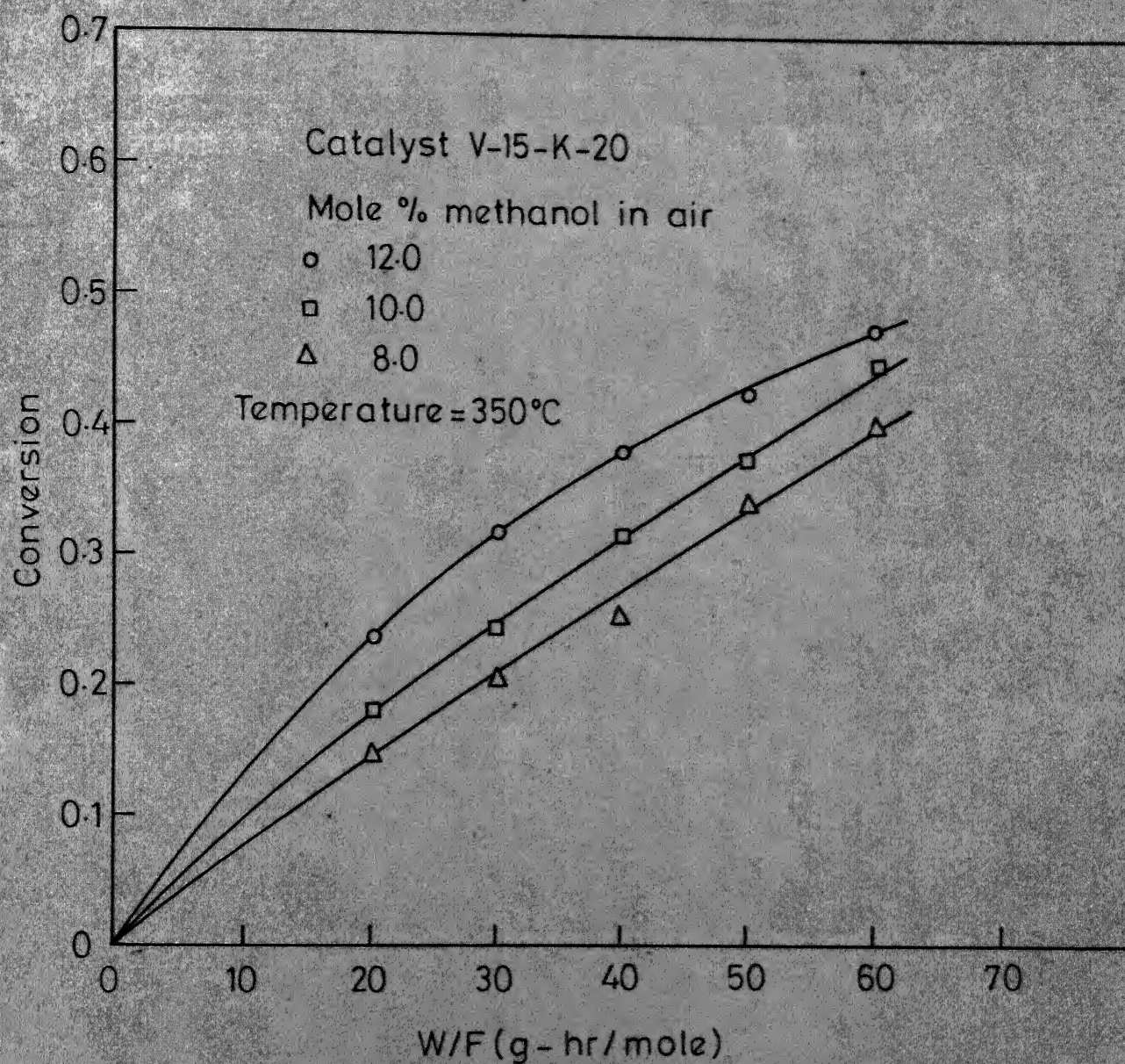


Fig. 6 - Effect of W/F on conversion of methanol for various methanol concentrations in the feed mixture.

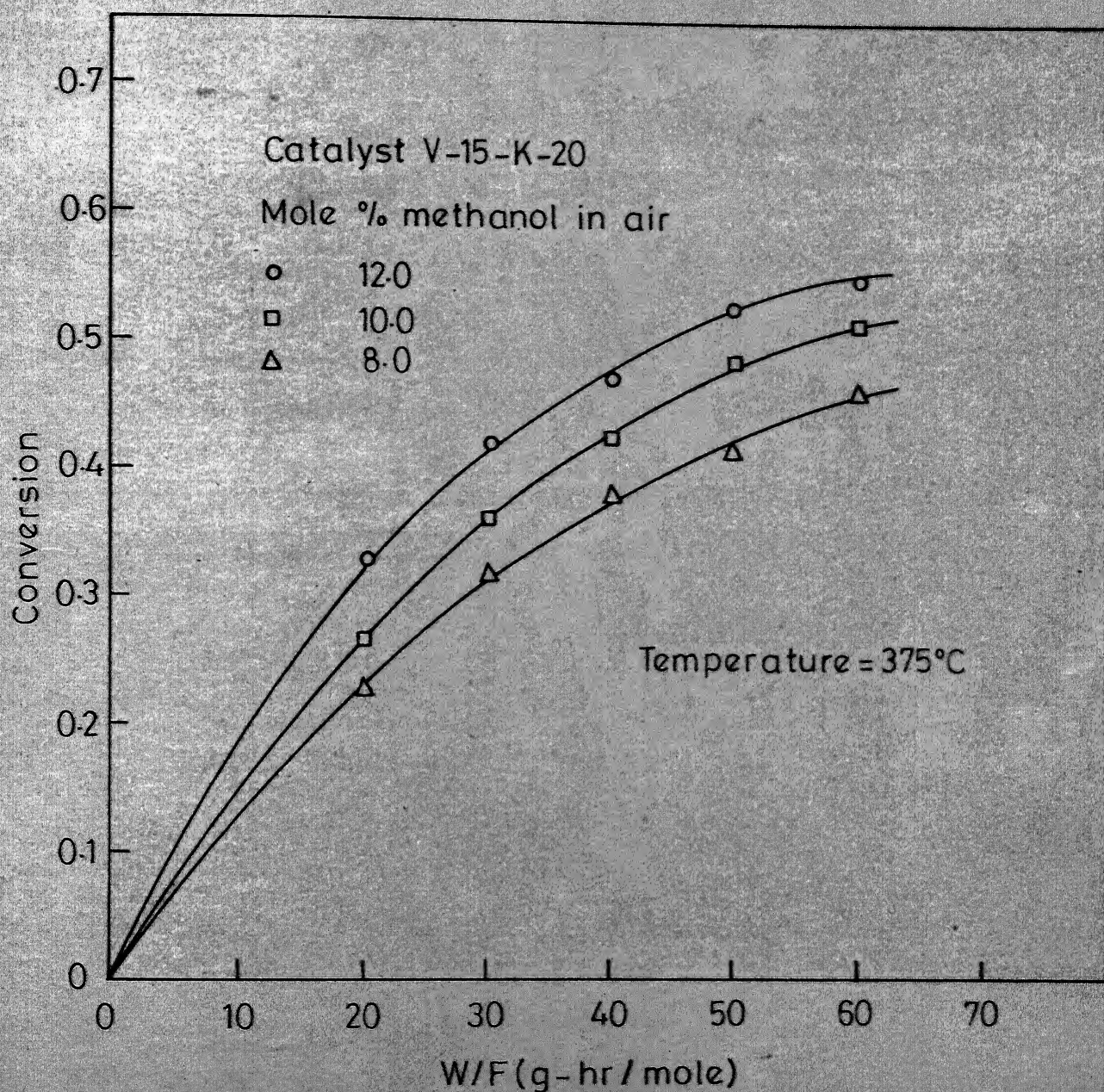


Fig. 7 - Effect of W/F on conversion of methanol for various methanol concentrations in the feed mixture.

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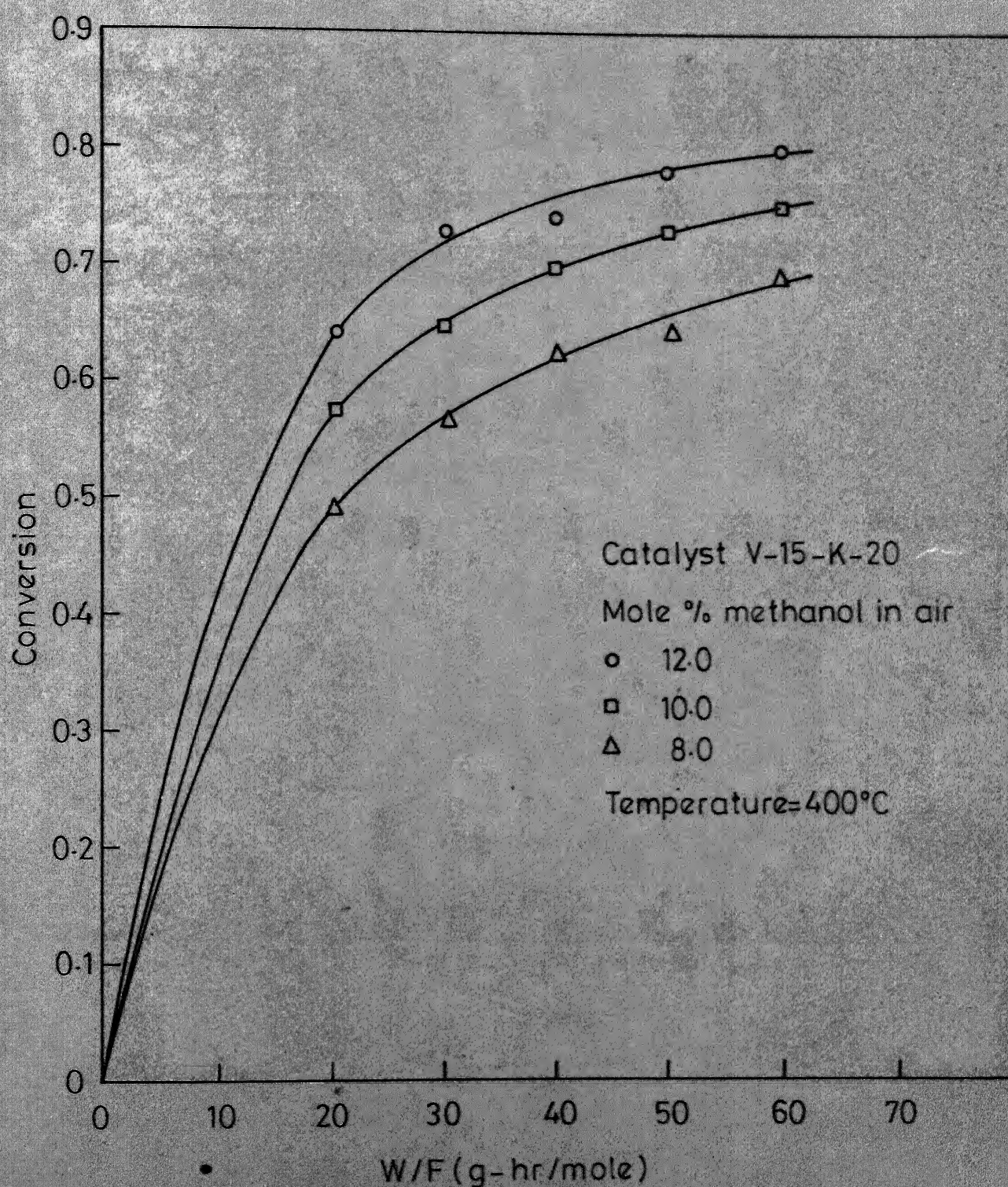


Fig. 8 - Effect of W/F on conversion of methanol for various methanol concentrations in the feed mixture.

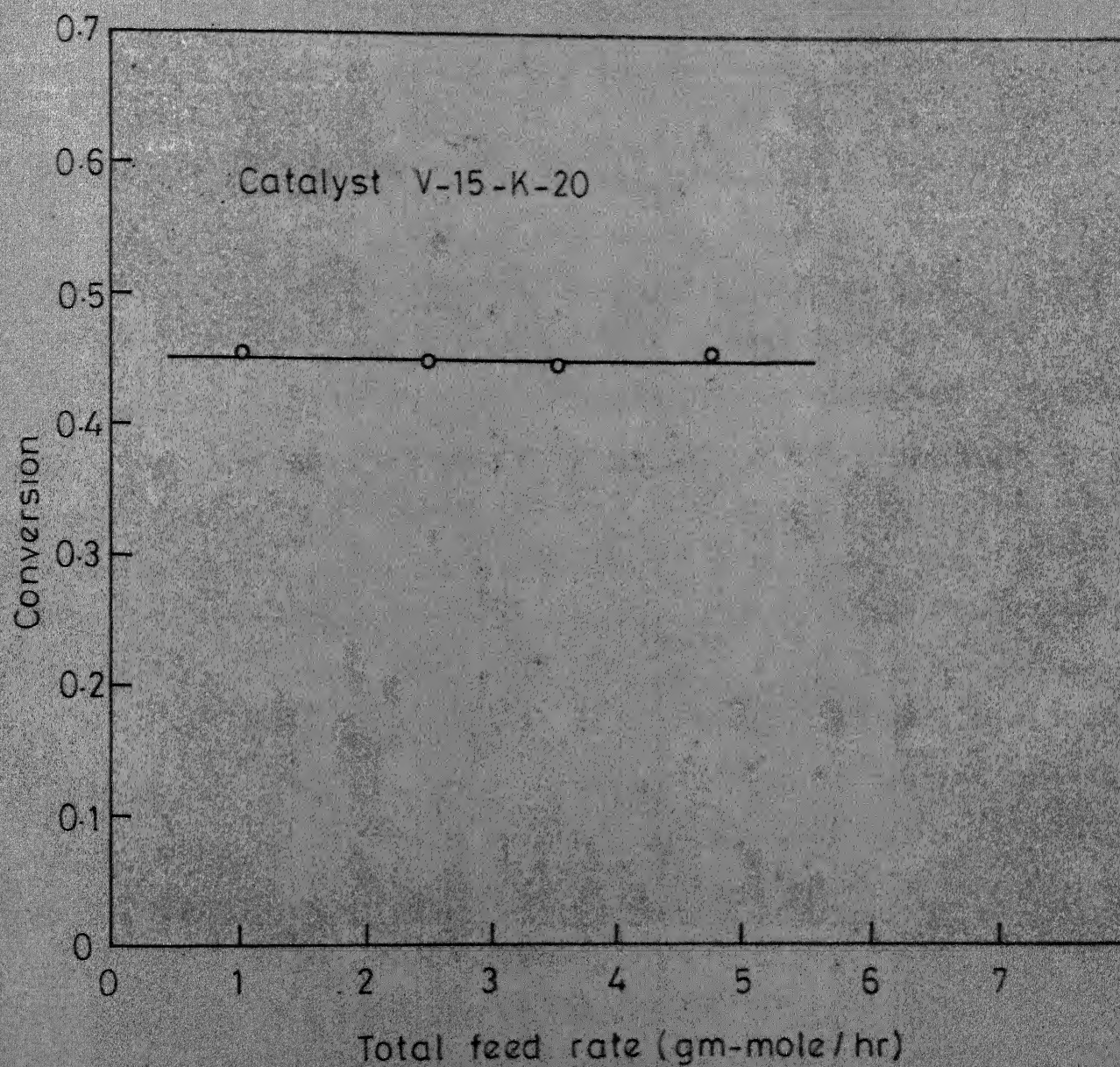


Fig. 9 - Effect of feed velocity on percentage conversion of methanol at 350°C, 10% methanol in air, $W/F = 40.0 \text{ g-hr / mole}$.

3.5 Kinetic Analysis:

In making a kinetic analysis of the experimental data an approach suggested by Hougan and Watson was used. The rate controlling mechanism of the solid catalysed gas reaction may be the mass transfer of the reactants or product or adsorption of reactant or desorption of products or the reaction of the adsorbed molecules at the catalyst surface.

The temperature and partial pressure gradient between the bulk fluid and the surface of the catalyst were evaluated by the method of Yoshida et al. [17]. The temperature difference across the film was less than 1°C and the partial pressure gradient was found to be of the order of 0.001 atm. Thus heat and mass transfer effects were insignificant and hence could be neglected.

The method of Young and Hougen [18] was used to eliminate some more of the rate controlling steps. A plot of initial ratio [Figure 10] against mole per cent of methanol indicated that the desorption of the product was definitely not rate controlling.

The changed in the color of the catalyst to black when only methanol was pass over it for short time and the possibility of $\text{V}_2\text{O}_5\text{-K}_2\text{SO}_4$ existing in a state of lower valency and similar kinetics studies of methanol oxidation carried out by others suggested the interpretation of the results of the kinetics measurements to be based on two stage redox mechanism

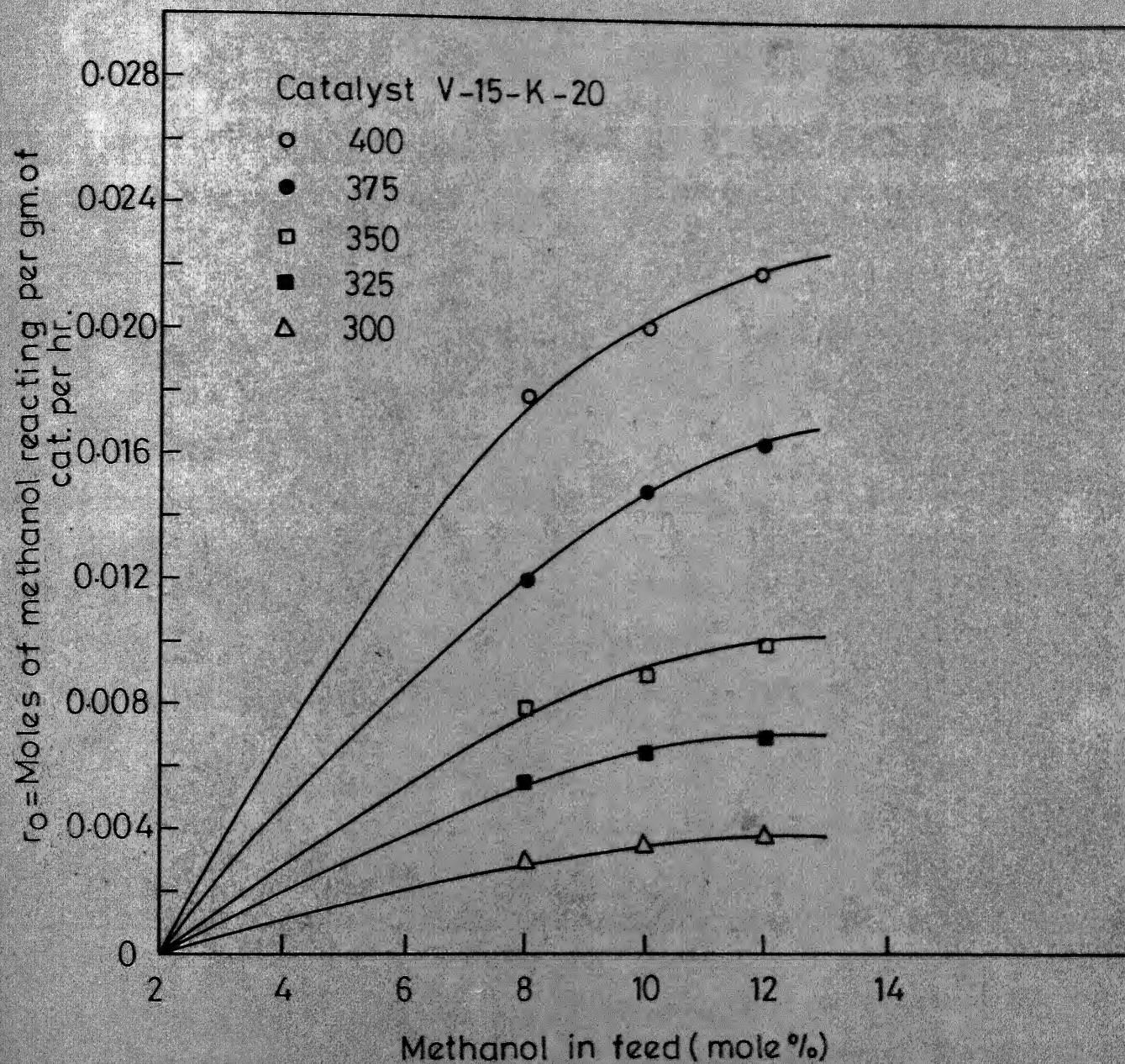
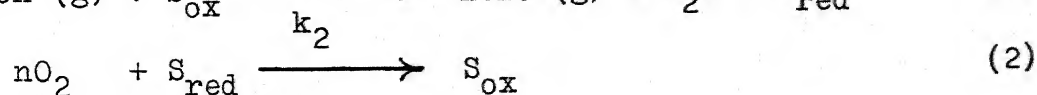
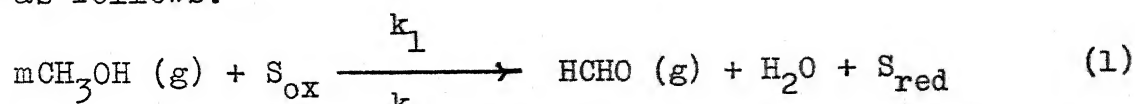


Fig. 10 -Initial ratio (r_0) vs. mole percentage methanol in air.

similar to one postulated by Mars and Van Krevelen [19].

Accordingly, the reaction can be expressed to be taking place as follows:



Assuming first order dependence of the rate reaction on the partial pressure of methanol (i.e. reduction of catalyst by methanol)

$$-\frac{dp_M}{dt} = k_1 p_M \theta \quad (3)$$

where θ is the fraction of surface occupied by oxygen.

With the similar assumption, the rate of second step (i.e. oxidation of the catalyst by oxygen)

$$-\frac{dp_{\text{O}_2}}{dt} = k_2 p_{\text{O}_2} (1 - \theta) \quad (4)$$

Under steady state

$$\alpha \left(\frac{dp_M}{dt} \right) = \frac{dp_{\text{O}_2}}{dt} \quad (5)$$

where α is the number of oxygen molecules required for converting one methanol mole to formaldehyde. Hence from equations (3), (4), and (5).

$$\begin{aligned} \alpha k_1 p_M \theta &= k_2 p_{\text{O}_2} (1 - \theta) \\ \theta &= \frac{k_2 p_{\text{O}_2}}{k_2 p_{\text{O}_2} + \alpha k_1 p_M} \end{aligned} \quad (6)$$

substituting the value of θ in equation (3)

$$r = \frac{k_1 k_2 p_M p_{O_2}}{k_2 p_{O_2} + \alpha k_1 p_M} \quad (7)$$

A more general rate equation may be written as

$$r = \frac{k_1 p_M^m}{1 + \left(\frac{\alpha k_1 p_M^m}{k_2 p_{O_2}^n} \right)} \quad (8)$$

where m and n are the reaction order with respect to methanol and oxygen respectively. Equation (8) was integrated for the integral flow reactor for various value of m and n between 0 and 1. These rate expressions are listed in Table 2.

Linear regression analysis of two stages redox models to obtain the least squares fit values of the kinetic constants were performed. The linear regressions of the rate equations were made at each temperature. The values are tabulated in Table 3.

All the five integrated rate equation for various value of m and n between 0 and 1 were examined. Rate expressions were eliminated from further considerations when either of the converged reaction constant k_1 or k_2 become negative. The constants for each model are defined.

TABLE 2

TWO STAGE REDOX MODEL

Model No.	Reaction CH_3OH	Order O_2	Integrated Rate Equations
1	1	0.5	$\frac{W}{F} \frac{\text{op}_M}{\ln(1-x)} = -\frac{1}{k_1} + \frac{4\alpha}{k_2} \frac{[\text{op}_{\text{O}_2}]^{1/2} - (\text{op}_{\text{O}_2} - \frac{1}{2} x \text{op}_M)^{1/2}}{\ln(1-x)}$
2	1	0	$\frac{W}{F} \frac{1}{x} = -k_1 \frac{\ln(1-x)}{\text{op}_M x} + \frac{\alpha}{k_2}$
3	0.5	0	$\frac{W}{F} \frac{1}{x} = \frac{2}{k_1} \frac{[1 - (1-x)^{1/2}]}{\text{op}_M^{1/2} x} + \frac{\alpha}{k_2}$
4	1	1	$\frac{W}{F} \frac{\text{op}_M}{\ln(1-x)} = -\frac{1}{k_1} + \frac{2\alpha}{k_2} \frac{\ln[\text{op}_{\text{O}_2}/(\text{op}_{\text{O}_2} - \frac{1}{2} \text{op}_M x)]}{\ln(1-x)}$
5	0.5	0.5	$\frac{W}{F} \frac{\text{op}_M^{1/2}}{[1 - (1-x)^{1/2}]} = \frac{2}{k_1} + \frac{4\alpha}{k_2} \frac{[\text{op}_{\text{O}_2}]^{1/2} - (\text{op}_{\text{O}_2} - \frac{1}{2} \text{op}_M x)^{1/2}}{[\text{op}_M]^{1/2} [1 - (1-x)^{1/2}]}$

TABLE 3RESULTS OF REGRESSION ANALYSIS

<u>Model No.1</u>	<u>$k_1 \times 10^{-5}$</u>	<u>$k_2 \times 10^{-5}$</u>
300°C	2.12	0.11
325°C	3.62	0.19
350°C	5.82	0.33
375°C	9.50	0.52
400°C	16.03	0.91
<u>Model No.2</u>	<u>$k_1 \times 10^{-6}$</u>	<u>$k_2 \times 10^{-6}$</u>
300°C	-1.0	0.2
325°C	-8.4	0.6
350°C	-132.9	1.0
375°C	47.5	1.3
400°C	855.5	2.0
<u>Model No.3</u>	<u>$k_1 \times 10^{-6}$</u>	<u>$k_2 \times 10^{-6}$</u>
300°C	-0.2	0.3
325°C	-2.2	0.6
350°C	-30.0	1.0
375°C	13.1	1.3
400°C	296.0	2.0
<u>Model No.4</u>	<u>$k_1 \times 10^{-6}$</u>	<u>$k_2 \times 10^{-6}$</u>
300°C	20.4	2.9
325°C	126.6	4.8
350°C	49.6	1.1
375°C	488.9	7.4
400°C	87.6	43.8

Table 3 (contd)

<u>Model No.5</u>	<u>$k_1 \times 10^{-6}$</u>	<u>$k_2 \times 10^{-6}$</u>
300°C	2.0	-0.02
325°C	4.5	-0.2
350°C	6.7	-1.5
375°C	9.5	1.7
400°C	14.7	-14.4

<u>Model No.</u>	<u>Constant</u>	<u>Slope</u>
1	$-\frac{1}{k_1}$	$\frac{4\alpha}{k_2}$
2	$\frac{\alpha}{k_2}$	$-\frac{1}{k_1}$
3	$\frac{\alpha}{k_2}$	$\frac{2}{k_1}$
4	$-\frac{1}{k_1}$	$\frac{2\alpha}{k_2}$
5	$\frac{2}{k_1}$	$\frac{4\alpha}{k_2}$

The experimental and calculated values are given in Table 4.

The following rate expression with $n=0.5$ and $m=1.0$ was found to give best possible fit to the experimental data.

$$r = \frac{k_1 p_M}{k_1 p_M + 1 + \left(\frac{p_M}{2k_2 p_{O_2}^{0.5}} \right)} \quad (9)$$

The deviation between the calculated values of W/F from the experimental values were less than 5 per cent.

3.6 Temperature Effect on Rate Constants:

The temperature dependence of the rate constant k_1 and k_2 was determined for temperature between 300 and 400°C. Figure 11 and 12 show the Arrhenius plots for k_1 and k_2 , respectively. The reaction followed the Arrhenius law in the temperature range studied and the following expressions were obtained for rate constants:

TABLE 4

COMPARISON BETWEEN THE EXPERIMENTAL AND CALCULATED
DATA

Model No.1

W/F (Experimental)	W/F (Calculated)	Present Deviation
<u>300°C</u>		
20.0	20.26	1.28
30.0	30.13	0.43
40.0	39.89	0.27
50.0	50.80	1.57
60.0	60.35	0.56
<u>325°C</u>		
20.0	20.33	1.62
30.0	30.12	0.39
40.0	40.23	0.57
50.0	50.78	1.53
60.0	60.83	1.36
<u>350°C</u>		
20.0	19.84	0.80
30.0	29.89	0.36
40.0	40.45	1.11
50.0	50.66	1.30
60.0	61.05	1.71

Table 4 (contd)

W/F (Experimental)	W/F (Calculated)	Present deviation
375°C		
20.0	20.41	2.00
30.0	30.48	1.56
40.0	39.68	0.80
50.0	51.02	1.98
60.0	60.80	1.31
400°C		
20.0	19.80	1.00
30.0	29.50	1.66
40.0	39.88	0.30
50.0	50.46	0.91
60.0	60.93	1.52

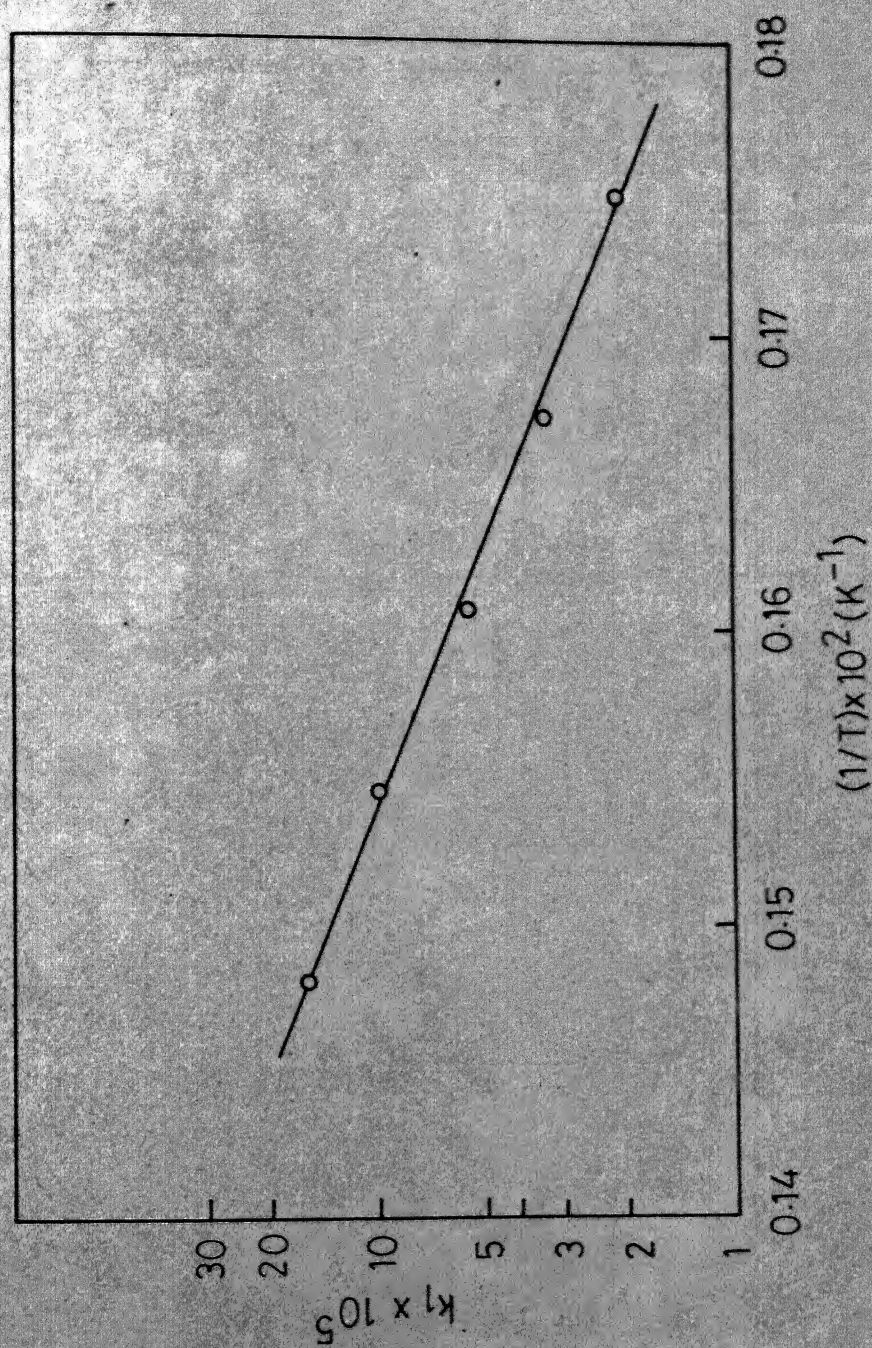


Fig. 11 - Temperature effect on rate constant k_1

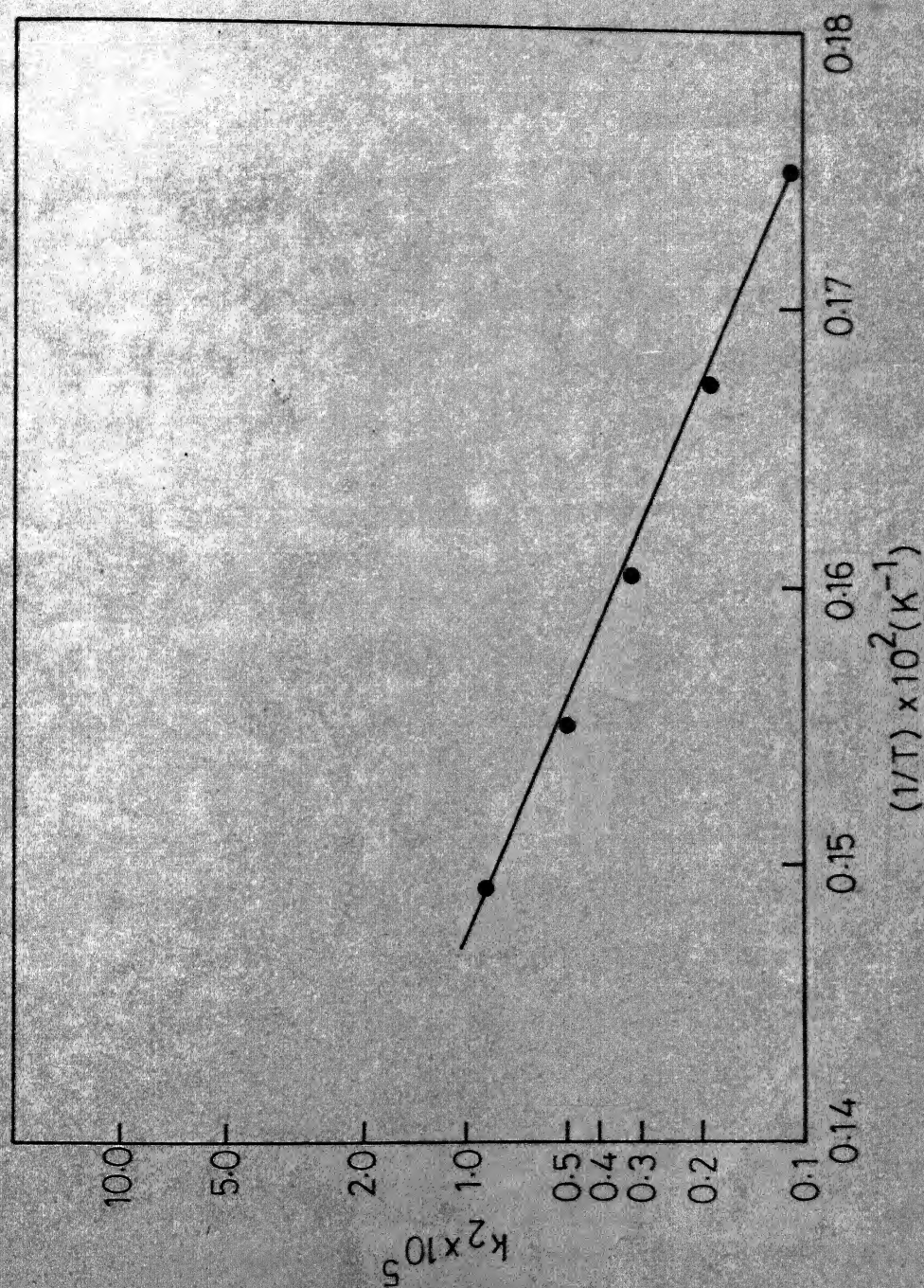


Fig. 12 - Temperature effect on rate constant k_2

$$\ln k_1 = 2.3373 - \frac{0.7511 \times 10^4}{T} \quad (10)$$

$$\ln k_2 = 3.2615 - \frac{0.8407 \times 10^4}{T} \quad (11)$$

The activation energies of the two steps (Equations 1 and 2) evaluated from equations (10 and 11) are 14.8 and 16.64 KCal/mole respectively. The values of the activation energy in each step is positive, indicating a satisfactory temperature relationship. These activation energies were found to be similar to those obtain by Agarwal [13].

The least square values of k_1 and k_2 at 300°C was found to be 2.12×10^{-5} moles/sec. (gm. catalyst) (atmosphere) and 0.11×10^{-5} moles/sec. (gm. cat.)(atm)^{0.5}, respectively.

The proposed rate equation can represent a modified Hinshelwood mechanism for a surface sparsely covered by one or both reactants. In that case, one or both constants then represent the product of a rate constant and an adsorption constant. The rate equation does not exclude the possibility that the reoxidation of partially reduced catalyst is realized by adsorbed oxygen. It is unlikely, however, that the required amount of oxygen available for methanol oxidation could be adsorbed oxygen on the n-type semi-conducting catalyst employed.

The strength of the V=O bond has been known to be a controlling factor for the catalytic activity. The promotive action of K_2SO_4 on V_2O_5 in the selective oxidation of methanol

to formaldehyde may be due to weakening of this bond by doping. Tarama et al. [12] have established from the 1025 to 1000 cm^{-1} bond which showed the promotive action for oxidation of carbon monoxide or hydrocarbons. This characteristic feature of the V=O bond was attributed to VOSO_4 or a similar compound formed by K_2SO_4 .

The general kinetics and mechanism of the reaction was found to be similar to these obtained by Jiru [6], Mann and Hahn [8], Mann and Dosi [9] and Bhattacharya [11].

CHAPTER 4

CONCLUSION

The catalytic oxidation of methanol over vanadium pentaoxide-potassium sulphate impregnated on silica gel was investigated between 300 and 400°C at atmospheric pressure for reciprocal space velocity (W/F) of 20.0 to 60.0 gm hr/gm mole for the methanol concentration on the feed of 3.0 to 12.0 per cent. The maximum yield of formaldehyde with 93 per cent selectivity and 80 per cent conversion of methanol was obtained at 400°C with a W/F ratio of 60.0 gm.hr/gm. mole and 12 per cent methanol in air. A two stage redox mechanism was used to derive the rate expression fitting the experimental data satisfactorily.

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NOMENCLATURE

P_m	Partial pressure of methanol in feed (atm.)
p_{O_2}	Partial pressure of oxygen in feed (atm.)
W	Weight of catalyst (gm)
F	Molal feed rate (Mole/hr)
T	Temperature, °C
W/F	Reciprocal of space velocity and space velocity is expressed as the number of cc of the total feed at NTP per unit volume of catalyst per sec.

Subscripts

m	Methanol
n	Oxygen

Greek Symbols

θ	Fraction of the catalyst surface covered by oxygen
α	Number of oxygen molecules needed to convert one molecule of methanol to formaldehyde.